1. Project Name:	**Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations**
2. Lead Organization:	Goodyear Chemical 1485 E. Archwood Ave, Bldg 132 Akron, OH 44316-3209
3. Principal Investigator:	Jeffrey Goodwin, Goodyear Chemical 330-796-7774 Phone 330-796-5293 FAX jagoodwin@goodyear.com
4. Project Partners:	Sandia National Laboratories Inter-Agency Work Order Material Modification Tina M. Nenoff 505-844-0340 tmnenof@sandia.gov Nofsinger Process & Industrial Group, a Division of Burns & McDonnell In-kind Contribution Process Modeling & Economic Evaluation Thomas M. Anderson 816-822-3275 tanders@burnsmcd.com
5. Date Project Initiated and FY of Effort:	April 23, 2002 -- April 23, 2003 FY1 and April 23, 2003 to-date – currently in FY2
6. Expected Completion Date:	April 23, 2005

7. Project Technical Milestones and Schedule:

Phase	Task	Task Description	Period	Contributor
I -III	0.0	General & Administrative	0-36	SNL, Gdyr, Nof
	1.1	Zeolite type versus carbon source deposition experiments	0-12	SNL
	1.2	Concurrent characterization of materials by TPD, surface area analysis, chemical analysis	0-12	SNL, Gdyr
	1.3	Concurrent C_5 separation experiments on materials that display selective adsorption of isoprene	0-12	SNL, Gdyr
	1.4	Selection of materials to be used in 1.5 *(Go/No-Go)*	12	SNL, Gdyr, Nof
I	1.5	Determine optimal temperature, flowrate, and feed concentration	13-20	SNL
	1.6	Determine best zeolite – carbon deposition condition combination via C5 separation experiments	20	SNL
	1.7	Selection of material to be used in 1.8 *(Go/No-Go)*	21	SNL, Gdyr, Nof
	1.8	Full material characterization by TPD, surface area analysis, chemical analysis, XRD, NMR, density measurement, and thermal analysis	21-24	SNL
	1.9	Synthesize sufficient quantity of material for use in II	21-24	SNL
	2.1	Pilot plant testing optimized carbon modified zeolite	25-30	Gdyr
	2.2	Analytical support for chemical characterization	26-30	SNL, Gdyr
II	2.3	Lifetime studies including regeneration & desorption	27-30	SNL, Gdyr
	2.4	Feedback of results to Sandia and Nofsinger (Go/No-Go)	30	Gdyr
	2.5	Begin engineering studies from preliminary results	30-35	Nof
	3.1	Detailed economic calculations	30-35	Nof
	3.2	Complete detailed computer process modeling simulations	30-35	Nof
III	3.3	Complete detailed economic benefits from adsorption technology	30-35	Nof
	3.4	Feedback of results to Sandia and Goodyear (Go/No-Go)	30-36	SNL, Gdyr, Nof
	3.5	Engineering analysis with regard to feasibility of membrane process	30-36	SNL, Gdyr, Nof

8. Past Project Milestones and Accomplishments:

- Held kick-off meeting at Sandia in Albuquerque, NM in July, 2002
- Held review meeting at Goodyear in Akron, OH in February, 2003 with both Goodyear Executive and Chemical Leadership Teams
- Constructed pilot plant unit at Goodyear (capable of evaluating packed beds, disks, and membrane tubes)and also at Sandia for C_5 separation experiments
- Modified numerous zeolites (including Y, ZSM-5, Beta) by varying cation-loading, surface-modifying temperatures and durations, Si/Al ratios, carbonization levels
- Modified materials were characterized and evaluated for separations using BET surface analyzer and Temperature Programmed Desorption (TPD) of branched & linear C_5 hydrocarbons. TPD was used to measure the catalytic acid sites and sorptive strengths by NH3 and pyridine sorption.
- Analytical methods completed for separation/permeation at Goodyear
- Conducted preliminary testing of separation abilities of various carbonized pellet disks in Goodyear flow reactor. Disk appears to be too porous and allowing all gases to pass through. Secondary growth procedures are needed to “plug” defect sites. Ongoing.
- Commenced synthesizing alumina-supported Zeolite Y and ZSM-5 materials, with subsequent surface modification (various cations and carbonization levels)

- Supported synthesized and modified materials will be sent to Goodyear for separation testing on flow unit
- Began separation experiment testing at Goodyear's pilot plant unit.

9. Planned Future Milestones:

See item #7.

10. Issues/Barriers:

The primary *technical hurdle* in this work is finding the precise combination of zeolite and carbon deposition parameters that will be successful for the separation of n-pentane from isoprene, and then n-pentane from isoamylenes. Additional potential *hurdles* relate to scale up and industrial usage, such as potential fouling, deactivation, and material regeneration. It is expected that increasingly complex feed-streams are likely to increase fouling and decrease the ability to regenerate the materials, but these will not be known quantities until actual industrial testing is initiated. In the worst case scenario, however, we anticipate that these materials can be regenerated and re-used in a similar manner as industrial zeolite catalysts.

Fortunately, successful preliminary work has indicated that this separation is possible using differential adsorption on a carbon-modified zeolite. Furthermore, a great deal of groundwork concerning carbon deposition in zeolites has already been performed,[1,2,3,4] allowing us to focus on a relatively small number of variables. Selective desorption can be an issue with some adsorbent materials, and it is recognized in this research that studies will need to be performed regarding this issue. However, based on previous work[1], these materials will possess significantly different adsorption energies such that both pressure and temperature can be readily used to achieve selective desorption, and therefore successful separations of the hydrocarbons considered in this project.

11. Intended Market and Commercialization Plans/Progress:

Commercialization of this technology relies on the research and development of novel modified zeolite materials for advanced energy efficient separation processes for the petroleum and chemical industries with the help of IMF and future OIT funding. Successful research and development of these materials and their final commercialization into separation processes is guaranteed with the ensemble of varying skills from this project team. These skills include the industrial separations expertise of Goodyear, the advanced industrial process modeling of Nofsinger, and the research and development expertise of Sandia. It is envisioned that the successful completion of this research will position this project team with a future OIT proposal, which will be used to completely develop a commercially viable process. The integration of materials research, process development, and engineering analysis, via direct feedback, will streamline commercialization of this

[1] J. Antes, Z. Hu, W. Zhang, and K.J. Huttinger, Carbon 37 (1999) 2031.
[2] H.S. Cerqueira, P. Ayrault, J. Datka, P. Magnoux, and M. Guisnet, Journal of Catalysis 196 (2000) 149.
[3] H.G. Karge, W. Niessen, and H. Bludau, Applied Catalysis A: General, 146 (1996) 339.
[4] P. Andy, D. Martin, M. Guisnet, R.G. Bell, and R.A. Catlow, J. Phys. Chem. B, 104 (2000) 4827.

technology. ***Current and potential collaborating strategies*** are inherent to this proposal because each industrial partner has different skill sets. It is expected that during the commercialization stages of an OIT-funded proposal, Pall Corporation will be a new team member. Their contribution in the future OIT proposal will be the adaptation of this technology to membrane based separations, while licensing strategies, economic analysis, and potential market barriers and will be addressed by all partners of this future OIT proposal. Finally, the necessary validation to other chemical industries for this technology will be twofold. The economic benefits obtained through the *minimization of energy and waste* under industrial process conditions will be demonstrated via economic modeling by Nofsinger, and the technical feasibility of this will be demonstrated via pilot-plant trials by Goodyear. After the completion of this IMF proposal, OIT funding will be sought for material development of process separations relying on pressure swing adsorption and membranes.

12. Patents, publications, presentations: (Please list number and reference, if applicable.)

- Provisional Patent filed by Sandia April 10, 2002 entitled "Enhanced Selectivity of Zeolites by Controlled Carbon Deposition"
- "Novel modified zeolites for energy-efficient hydrocarbon separations." Ulutagay-Kartin M, Thoma S, Cornelius C, Nenoff TM. Abstracts of Papers of the American Chemical Society, v. 224(pt.1) pp. U439-U440 Aug. 18, 2002
- Attended and presented (poster and talk) at the DOE/OIT/IMF annual review meeting (Albuquerque, NM)
- Attended and presented (oral presentation) at the American Chemical Society National Fall Meeting in Boston, MA.
- Attended and presented (poster) at 3rd NLCAT'2002 Meeting, PNNL, Richland, WA, May 23, 2002
- Sandia (and Goodyear team members) presented a status overview to the Executive Team and the Chemical Senior Leadership Team of The Goodyear Tire & Rubber Company in February 2003 at Goodyear Corporate Headquarters in Akron, Ohio.

Industrial Materials For The Future
Project Fact Sheet

Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations

Benefits

Development of the proposed technology will benefit domestic isoprene processing (Goodyear produces approximately 60% of all domestic isoprene) but may also be extended to other hydrocarbon separation processes throughout the petroleum and chemical industries.

The annual benefit to industry are estimated:

- 64 trillion Btu/year in energy savings and
- A 2400 ton increase in synthetic zeolite manufacturing.

Zeolites as adsorbents are quickly becoming the technology of choice for the petroleum and chemical industry for reduction in environmental emissions, mainly volatile arganic compounds. Zeolites are finding broad applications in industry, especially in environmentally sensitive industrial processes.

Applications

The technology is applicable in the

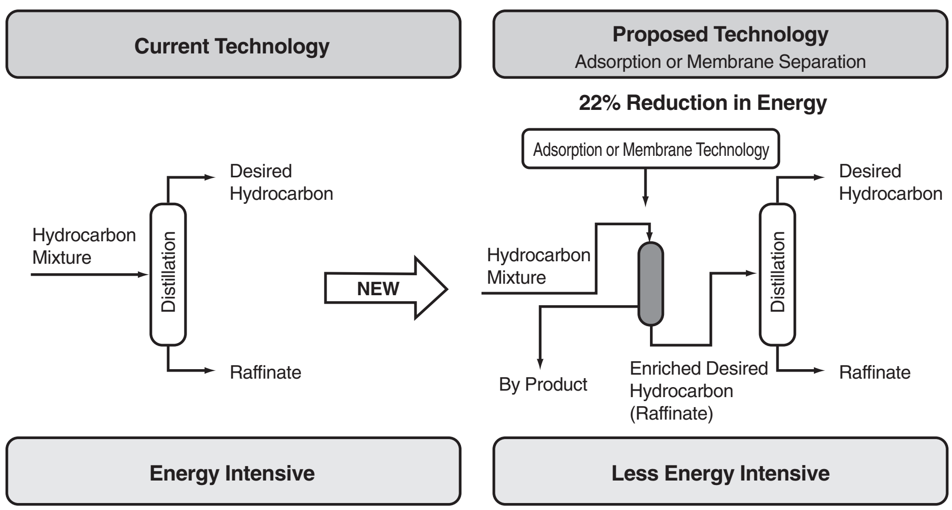
- **Chemical** and
- **Petrochemcial** industries.

The impact will result in improved production efficiencies of isoprene and also in the more efficient separation of other hydrocarbons.

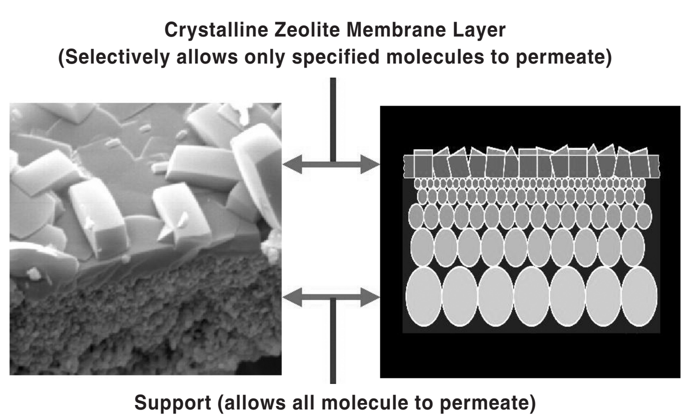
Zeolite separation technology can enable more efficient production of hydrocarbons

It is anticipated that this project will provide the next generation in separation technology. These materials are designed to minimize the energy consumption and raw materials associated with current separation processes by differentiating between olefins and alkanes, and between branched and linear hydrocarbons based upon differences in adsorption properties and molecule size.

Novel modified zeolites for energy-efficient hydrocarbon separations will be developed in this project. Controlled surface and framework modification of zeolites is the focus. A successful research project will create an enabling technology for future adsorbents, materials for membranes, and the potential development of shape-selective catalysts.



Current vs proposed hybrid technology for the separation of isoprene from a C5 mixture.



Zeolites as membranes

Project Description

Goal: The goals of this project are to
– Develop methods to selectively modify the sorptive properties of known zeolites.
– Create new adsorbents by modification of known zeolites.
– Allow adsorbent-based hydrocarbons separation processes to replace energy-intensive and energy inefficient processes such as distillation.
– Create the basis of a predictive model so that, via this technology, adsorbents may be tailored for particular processes.

Issues: During the last two decades, the domestic industry has performed limited research and development into the area of controlled surface and framework modification of zeolites for adsorption and membrane-based hydrocarbon separations. The successes associated with the research and development of zeolite modification for hydrocarbon has been limited because of the large technological gap between the novel material developers and the requirements of the hydrocarbon-processing industry.

This project will require the development of carbon-modified zeolites to allow new and energy-efficient adsorption-based separations. This effort is based on successful preliminary work performed.

Approach: The project is divided into three major phases. The first phase is to determine the relationship between zeolite type and carbon source and to optimize carbon deposition parameters. The second phase is to complete industrial pilot plant testing of carbon modified zeolites. The third phase is to perform engineering analysis and feedback of the proposed technology. The tasks include
– Determining zeolite type and carbon source relationships,
– Industrial pilot plant testing of carbon modified zeolites, and
– Engineering analysis and feedback.

Potential payoff: Currently, olefins are prepared by catalytic thermal cracking of saturated hydrocarbons. In the United States alone, 53 billion pounds of ethylene, 39 billion pounds of propylene, 4 billion pounds of butadiene, and 435 million pounds of isoprene are produced annually. The use of zeolites can have significant benefits on the energy efficiency of these processes.

This affords a huge opportunity to develop materials that will advance the current state of the art in hydrocarbon separations based on adsorbents and membranes. These separation technologies could result in a 22% reduction in energy for the aforementioned hydrocarbon purifications, which translates into an energy savings of 64 trillion Btu/year.

Progress and Milestones

- Characterize materials by surface area and chemical analysis.
- Perform separation experiments on materials that display selective adsorption of isoprene.
- Determine best zeolite-carbon deposition condition combination via separation experiments.
- Synthesize a sufficient quantity of material for testing.
- Test optimized carbon modified zeolite in a pilot plant.
- Conduct lifetime studies, including regeneration and desorption.
- Begin engineering studies from preliminary results.
- Complete detailed computer process modeling simulations.
- Complete engineering analysis with regard to feasibility of membrane process.

ORNL 2002-02427/jcn

imf

Primary

Goodyear Chemical
Akron, OH

Project Partners

Nofsinger Process and Industrial Group, a Division of Burns & McDonnell
Kansas City, MO

Sandia National Laboratories
Albuquerque, NM

For Additional Information, Please Contact

Charles A. Sorrell
Office of Industrial Technologies
Phone: (202) 586-1514
Fax: (202) 586-7114
Charles.Sorrell@ee.doe.gov

Mike Soboroff
Office of Industrial Technologies
Phone: (202) 586-4936
Fax: (202) 586-7114
Mike.Soboroff@ee.doe.gov

Visit our home page at
http://www.oit.doe.gov/imf/

Office of Industrial Technologies
Energy Efficiency
And Renewable Energy
U.S. Department of Energy
Washington, DC 20585
http://www.oit.doe.gov

OIT

January 2002